PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to the Manufacture of Fluorine Derivatives of Aliphatic Hydrocarbons

We, FRED DAVISON LEICESTER, of Halsmead, Mill Lane, St. Helens, Lancashire, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in the manufacture of halogenated compounds and more particularly to the manufacture of fluoro derivatives of the lower aliphatic hydrocarbons, e.g. methane and ethane.

It has already been proposed to manufacture fluorinated derivatives of methane by reacting hydrogen fluoride with carbon tetrachloride vapour in the presence of antimony chlorides supported on coke. Active charcoal has also been proposed as a catalyst. It has been proposed further, to prepare fluorine derivatives of acyclic hydrocarbons by reacting an acyclic hydrocarbon halide (other than fluoride) with hydrogen fluoride in the presence of a metallic halide catalyst which has the property of mutually exchanging its halogen with hydrogen fluoride, and whose fluoride has the property of mutually exchanging halogen with an acyclic hydrocarbon halogen derivative.

We have now found that fluoro derivatives of the lower aliphatic hydrocarbons can be prepared in a very efficient manner by reacting hydrogen fluoride at an elevated temperature and in the presence of a chromium halide, with the vapours of a halogen derivative of such a hydrocarbon, which contains at least one halogen atom other than fluorine. Typical halogen derivatives which are suitable are carbon tetrachloride or tetrachlormethane, trichloromethane, dichlorodifluoromethane etc. A suitable chromium halide for use in the reactions is chromic chloride supported on carbon in a massive or granular form. Preferably an excess of the halogen derivative of the hydrocarbon is employed for convenience in control, and the temperature in the reaction zone maintained at about 350—450° C.

A suitable catalyst may be prepared by soaking the carbon support, e.g. charcoal or coke, in an aqueous solution of the chromic chloride, preferably acidified by addition of hydrochloric acid, and then drying the coke in vacuo or in a stream of an inert gas at a raised temperature. The proportion of chromium salt to carbon may be varied in any convenient manner, such as for example, by altering the concentration of the impregnating solution or by subjecting the carbon to more than one impregnation with a saturated solution, and drying it after each impregnation.

The reaction products may be treated to isolate the fluoro derivatives from unconverted materials and by-products, e.g. by selective absorption in suitable solvents, or by liquefaction and fractional distillation; fractional cooling may also be used to effect the separation. Thus, the hydrogen halide produced in the reaction, together with unreacted hydrogen fluoride, may be removed by absorption in water and/or aqueous alkali maintained above the boiling point of the fluoro derivatives, the off-gases dried, and then condensed. Normally, a mixture of fluoro derivatives is obtained, e.g. where carbon tetrachloride is the original halogen derivative a number of fluoro-chloro derivatives of methane may be formed; these various compounds can be separated from each other and from excess of the carbon tetrachloride by fractional distillation or otherwise, and the unchanged carbon tetrachloride returned to the reaction chamber, together with more hydrogen fluoride.

In one form of the invention, chlorofluoro derivatives of methane are prepared by passing vapours of carbon tetrachloride together with hydrofluoric acid over granular coke impregnated with 5% of chromic chloride prepared as described above, the reaction chamber being maintained at about 400° C. Under such conditions the exit gases will contain hydrogen chloride, unreacted hydrofluoric acid gas and/or carbon tetrachloride, and various proportions of CF_2Cl_2, $CFCl_3$

CF_2Cl_2 and $CFCl_3$. The proportions of the original reactants will determine to a large extent the proportions and the constituents in the final mixture. The acids may be removed by washing successively with water and caustic soda solution, the gases dried by contact with concentrated sulphuric acid, each of these reagents being maintained at about 50° C. in order that the fluoro methanes shall not be condensed. The dried exit gases are then condensed by cooling to about −50° C. and fractionated.

EXAMPLE.

Coke broken to pass a ¼" mesh but not a 1/5" mesh was impregnated with 5% of its weight of chromic chloride, and dried in a current of nitrogen at 450° C. Anhydrous hydrogen fluoride was bubbled through carbon tetrachloride heated to 68—70° C. to obtain a mixture of the reactant vapours containing about 20% by volume of hydrogen fluoride. This mixture was passed over the catalyst in a chamber at 400° C. the time of contact being 20 secs. The exit gases were first cooled to 0° C. and excess carbon tetrachloride together with some $CFCl_3$ thereby condensed out, then scrubbed successively with water, dilute caustic soda solution, and concentrated sulphuric acid and the residual $CFCl_3$, CF_2Cl_2 and any remaining CCl_4 condensed by cooling to −50° C.

Dated the 2nd day of January, 1936.

WILLIAM MORRIS,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Fluorine Derivatives of Aliphatic Hydrocarbons

We, FRED DAVISON LEICESTER, of Halsmead, Mill Lane, St. Helens, Lancashire, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the manufacture of halogenated compounds and more particularly to the manufacture of fluoro derivatives of the lower aliphatic hydrocarbons containing not more than three carbon atoms, e.g. methane, ethane and propane.

It has already been proposed to manufacture fluorinated derivatives of methane by reacting hydrogen fluoride with carbon tetrachloride vapour in the presence of antimony chlorides supported on coke. Active charcoal has also been proposed as a catalyst. It has also been proposed in Specification No. 391,168 to prepare fluorine derivatives of acyclic hydrocarbons by reacting an acyclic hydrocarbon halide (other than fluoride) with hydrogen fluoride in the presence of a metallic halide catalyst which has the property of mutually exchanging its halogen with hydrogen fluoride, and whose fluoride has the property of mutually exchanging halogen with an acyclic hydrocarbon halogen derivative.

Antimony halides are disclosed in the above numbered specification as suitable catalysts, being desirably used in the liquid state. In Specification No. 428,361, a patent of addition to the before-mentioned patent, the use of halides of copper, silver, gold, zinc, cadmium, mercury, vanadium, manganese, iron, cobalt, nickel and platinum, which may be carried on an absorbent solid body, is described.

We have now found that, although chromium fluoride has no substantial action upon halogen derivatives of acyclic hydrocarbons in the absence of hydrogen fluoride, chromium halides are nevertheless, effective catalysts for the production of fluorinated hydrocarbons from hydrogen fluoride and halogenated derivatives of hydrocarbons.

According to the present invention fluoro derivatives of hydrocarbons are manufactured by reacting hydrogen fluoride at an elevated temperature and in the presence of a chromium halide with the vapour of a saturated halogen derivative of a lower aliphatic hydrocarbon containing not more than three carbon atoms and containing at least one halogen atom other than fluorine. Typical derivatives include tetrachloromethane (carbon tetrachloride), trichloromethane, monofluorotrichloromethane, and tetrachloroethane. Suitable chromium halides for use in the reaction are chromic chloride and chromic fluoride supported on carbon in a massive or granular form. In some cases the chromium halide may also be associated with the oxide. A suitable temperature at which to carry out the reaction is 350—550° C. depending on the catalyst and the derivative it is desired to prepare.

A suitable catalyst may be prepared by soaking a carbon support, e.g. charcoal or coke, in an aqueous solution of chromic chloride, preferably acidified by addition of hydrochloric acid, and then drying in vacuo, or in a stream of an inert gas at a raised temperature. The proportion of chromium salt to carbon may be varied in any convenient manner, such as, for example, by altering the concentration of the impregnating solution or by subjecting the carbon to more than one impregnation with a saturated solution, and drying it after each impregnation. A chromium fluoride catalyst may be prepared by treating freshly precipitated chromic hydroxide with aqueous hydrogen fluoride, pasting the product on granulated coke, and drying the mixture in a current of inert gas, e.g. nitrogen, at temperatures of 400—600° C.

We find that the extent to which fluorination of the hydrocarbon halide takes place increases with increasing temperature, and with increasing proportion of hydrogen fluoride to hydrocarbon halide. We prefer to work with an excess of the hydrocarbon halide, since under such circumstances it is easier to control the composition of the reaction products (by varying the temperature and the magnitude of the excess) and to free them from unconverted materials in an economical and convenient manner. However, in preparing the more highly fluorinated derivatives it may not be feasible to produce satisfactory yields unless a large proportion of hydrogen fluoride is used.

The reaction products may be treated to isolate the fluoro derivatives from unconverted materials and by-products, e.g. by selective absorption in suitable solvents, or by liquefaction and fractional distillation or by fractional condensation of the reaction products or by a combination of these methods. Thus, the hydrogen halide produced in the reaction, together with unreacted hydrogen fluoride, may be removed by absorption in water and/or aqueous alkali maintained above the boiling point of the fluoro derivatives after which the gases are dried and then condensed. Normally a mixture of fluoro derivatives is obtained, e.g. when carbon tetrachloride is the original halogen derivative a number of fluoro-chloro derivatives of methane may be formed; these various compounds can be separated from each other and from excess of the carbon tetrachloride by fractional distillation or otherwise, and the unchanged carbon tetrachloride returned to the reaction together with more hydrogen fluoride.

Where the object is to produce a particular fluorine derivative containing more than one fluorine atom per molecule, any fluorinated compounds containing less than the desired number of fluorine atoms per molecule may also be returned to the reaction.

The invention will be further described with reference to the manufacture of chlorofluoro derivatives of methane by reacting carbon tetrachloride with hydrogen fluoride, though it will be understood that our invention is not limited to the use of this particular starting material.

In carrying out this form of our invention chlorofluoro derivatives of methane are prepared by passing vapours of carbon tetrachloride and hydrofluoric acid through a reaction tube containing a chromium halide catalyst, which may be prepared by one of the methods described above.

The reaction mixture of hydrogen fluoride and carbon tetrachloride can be obtained in a convenient manner by bubbling the hydrogen fluoride into a bulk of carbon tetrachloride maintained at a suitable temperature, and by varying this temperature the proportion of the two constituents may be varied. Thus, for example, if the temperature of the carbon tetrachloride is 79° C. the ratio (by volume) of the hydrogen fluoride to the carbon tetrachloride in the mixed vapour is 0.23:1, while if the temperature is lowered to 53° C. the ratio becomes 1.20:1.

The reaction temperature used, must, of course, be less than the melting point of chromium halide. From this point of view it may approach 600° C. if chromium fluoride is used, but temperatures above about 550° C. are not suitable when the catalyst is chromium chloride. The effect of the temperature on the hydrocarbon derivatives must also be considered. In the case of carbon tetrachloride for instance, decomposition commences above about 550° C. with the formation of hexachlorethane. The choice of suitable temperature will also be influenced by the particular derivative it is desired to prepare since the formation of those derivatives containing a lower number fluorine atoms will be favoured by a lower temperature. For practical purposes, however, we find that the rate of reaction below about 400° C. is too low for effective conversion.

The reaction time necessary is also dependent on the temperature of the catalyst and on the particular derivative which it is desired to produce, lower temperatures and the more highly fluorinated compounds requiring the longer times. In general we find that at temperatures of between 400° and 550° C.

contact times of 15 to 25 seconds will furnish satisfactory yields.

The exit gases from the catalyst chamber will contain hydrogen chloride, unreacted hydrofluoric acid gas and/or carbon tetrachloride together with various proportions of $CFCl_3$, CF_2Cl_2, CF_3Cl and CF_4. The acids may be removed by washing successively with water and caustic soda solution and the gases dried by contact with concentrated sulphuric acid, each of these reagents being maintained at about 50° C. in order that the fluoromethanes shall not be condensed. The dried exit gases may be then liquefied by cooling to about −50° C. and fractioned. Alternatively any carbon tetrachloride present and any monofluorotrichloromethane may be removed directly (either separately or together) from the exit gases by means of one or more condensing columns working at appropriate temperatures, and the acids subsequently removed before condensing the remaining fluorinated hydrocarbons.

The following examples illustrate our invention:—

EXAMPLE 1.

To prepare the catalyst coke broken to pass a ¼" mesh and stay on a 1/5" mesh was impregnated with 5% of its weight of chromic chloride, and dried in a current of nitrogen at 450° C. Gaseous hydrogen fluoride was bubbled through carbon tetrachloride heated to 68—70° C. to obtain a mixture of reactant vapours containing about 20% by volume of hydrogen fluoride. This mixture was passed over the catalyst in a chamber at 400° C. the time of contact being 20 secs. The exit gases were first cooled to 0° C. to condense as much as possible of the excess carbon tetrachloride together with some $CFCl_3$ and then scrubbed successively with water, dilute caustic soda solution, and concentrated sulphuric acid. The residual $CFCl_3$, CF_2Cl_2 and any remaining CCl_4 were finally condensed by cooling to −50° C.

EXAMPLE 2.

A chromium fluoride catalyst was prepared by treating 158 parts by weight of chromic chloride with excess aqueous ammonia. The precipitated chromium hydroxide was washed with water and the product treated with 100 parts by weight of 60% aqueous hydrofluoric acid. The coke (1/8"—1/16" mesh) was pasted with this chromium fluoride to give a catalyst containing 15% by weight of chromium fluoride and the whole was dried out in a nickel catalyst tube in a current of nitrogen for 4—5 hours at 450° C. Over this catalyst maintained at 550° C. was passed a mixture of hydrogen fluoride and carbon tetrachloride, the proportion of the former to the latter being 0.23:1 by volume, and the time of contact with the catalyst being 20 secs. The off-gases were washed with water and caustic soda solution, dried with sulphuric acid, each of these reagents being maintained at 50° C., and condensed at −50° C. On analysis the gases were found to have the following constitution:

CF_2Cl_2	- -	47.2% by weight
$CFCl_3$	- -	45.9% ,, ,,
CCl_4	- -	6.9% ,, ,,

The conversion of hydrofluoric acid to fluorinated hydrocarbons was practically 100%.

EXAMPLE 3.

The process of Example 2 was repeated using a catalyst temperature of 450° C. The condensed gases had the following composition:

CF_2Cl_2	- -	33.4% by weight
$CFCl_3$	- -	60.6% ,, ,,
CCl_4	- -	5.9% ,, ,,

Practically complete conversion of the hydrogen fluoride was attained.

EXAMPLE 4.

The process of Example 2 was repeated, the ratio HF/CCl_4 being 1.20:1. The gases had the following composition:

CF_2Cl_2	- -	82.1% by weight
$CFCl_3$	- -	17.9% ,, ,,
CCl_4	- -	trace.

EXAMPLE 5.

A mixture of HF and CCl_4 vapour in the ratio of 2.0:1 was passed over a chromium fluoride catalyst prepared as in Example 2, and maintained at 550° C., the time of contact with the catalyst being 20 secs. The gases were collected as in Example 2, and had the following composition:

CF_3Cl	- -	8.1% by weight
CF_2Cl_2	- -	67.8% ,, ,,
$CFCl_3$	- -	24.1% ,, ,,
CCl_4	- -	trace.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the preparation of fluoroderivatives of hydrocarbons which comprises reacting hydrogen fluoride at an elevated temperature and in the presence of a chromium halide with the vapour of

a saturated halogen derivative of a lower aliphatic hydrocarbon containing not more than three carbon atoms and at least one halogen atom other than fluorine.

2. Process as claimed in Claim 1 in which the chromium halide is chromium fluoride.

3. Process for the preparation of fluoro-derivatives of methane which comprises reacting hydrofluoric acid at an elevated temperature and in the presence of a chromium halide with the vapour of carbon tetrachloride.

4. Process as claimed in Claim 3 in which the chromium halide is chromium fluoride.

5. Process as claimed in Claims 1, 2, 3 or 4 in which the reaction is carried out at a temperature of 350°—550° C.

6. Process as claimed in Claims 3 or 4 in which the reaction is carried out at a temperature of 400°—550° C., the time of contact of the vapours with the catalyst being 15—25 seconds.

7. Process for the preparation of fluoro-derivatives of hydrocarbons substantially as hereinbefore described.

8. Fluoro-derivatives of hydrocarbons whenever prepared by the processes claimed in any of the preceding claims or by their obvious chemical equivalents.

Dated this 4th day of January, 1936.

WILLIAM MORRIS,
Solicitor for the Applicants.

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